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Improved Method for Measuring Aerosol Strong Acidity Results from a Nine-Month Study in St. Louis, Missouri and Kingston, Tennessee

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16. ABSTRACT

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AN IMPROVED METHOD FOR MEASURING AEROSOL STRONG ACIDITY: RESULTS FROM A NINE-MONTH STUDY IN ST LOUIS, MISSOURI AND KINGSTON, TENNESSEE

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Abstract—An improved method for measuring strong acidity of atmospheric aerosols is presented. An ammonia diffusion denuder was developed to prevent neutralization of the acidic aerosol samples. In addition, a new procedure for protecting samples during shipment and analysis was used. An increase in the sensitivity of the analysis was achieved by extraction of the aerosol sample in a small solution volume, 3 ml, of 10^{-4} N $HClO_4$, and the use of a microelectrode for pH determination. Finally, results from a nine-month study in St Louis, Missouri and Kingston, Tennessee are given.

Key word index: Acid aerosols, ammonia, ammonium bisulfate, ammonium sulfate, diffusion denuder, letovicite, nitrogen oxides, ozone, sulfates, sulfuric acid, sulfur dioxide.

INTRODUCTION

The oxidation of the major air pollutants SO_2 and NO_x through either homogeneous (gas phase) or heterogeneous (gas/particle phase) processes, results in the formation of acidic gases and aerosols. Primary products of these oxidation reactions, sulfuric and nitric acid, have potentially significant adverse impacts not only on the atmospheric environment, but also on the entire ecosystem. Under usual atmospheric conditions, H_2SO_4 nucleates with water vapor (Kiang *et al.*, 1973). However, HNO_3 is in the gas phase at relative humidities (RHs) < 98% (Nair *et al.*, 1983). H_2SO_4 as well as HNO_3, can be neutralized by atmospheric NH_3. Hydrogen ions, from the dissociation of H_2SO_4 and bisulfate ion in the aerosol droplets, react with the NH_3 to form ammonium ions. Depending on the aerosol droplet composition and RH, the partly or entirely neutralized sulfates will remain in the liquid phase or change to the solid phase. Also, it is possible for an aerosol particle to contain both phases, where the partition between solid and liquid phase is given by the solubility diagram of the system: H_2O-$[NH_4]_2SO_4$-H_2SO_4 (Tang *et al.*, 1978). Depending on the ratio of NH_4^+/SO_4^{2-}, the solid phase of the sulfate aerosol particles consists of either: ammonium sulfate; ammonium sulfate and letovicite; letovicite; letovicite and ammonium bisulfate; or ammonium bisulfate. While NH_3 is scavenged by acidic sulfate aerosols until neutralization is achieved, it presents a substantial vapor pressure over ammonium nitrate particles. The ammonium nitrate aerosol dissociation constant, $K = [P_{HNO_3}][P_{NH_3}]$, depends on the aerosol pH, temperature, and RH (Tang, 1980; Stelson and Seinfeld, 1982). Finally, assuming that there is no mechanism preventing the neutralization of acid aerosols by NH_3, the presence of acidic particles implies that for humidity below $\approx 98\%$, HNO_3 is almost all in the gas phase. Therefore, the aerosol strong acidity is nearly all due to acid sulfates.

It is well established that atmospheric aerosols are at times acidic (Brosset *et al.*, 1975; Stevens *et al.*, 1980; Pierson *et al.*, 1980; Tanner *et al.*, 1984; Ferek *et al.*, 1983; Spengler *et al.*, 1986). However, most of the studies have been of short duration. A notable exception was the intensive Sulfate Regional Experiment (SURE), sponsored by the Electric Power Research Institute (EPRI, 1983). Through those studies the temporal and spatial patterns of both sulfate concentrations and wet and dry deposition were recognized. The region of eastern Ohio and western Pennsylvania has the lowest pH rainfall in the United States (Pierson *et al.*, 1987). This region also has the highest annual sulfate particle concentrations (Altshuller, 1980; Wilson *et al.*, 1981). While elevated particle sulfate events occur on a regional scale, there is subregional variation in aerosol acidity due to partial or complete neutralization by ambient NH_3, as shown by the New York Summer Aerosol Study (Lioy *et al.*, 1980).

In addition to the effects of acidic particles on the environment, vegetation and aquatic life, there are possible direct human respiratory effects due to these particles (Schlesinger *et al.*, 1983; Lippmann, 1985; Holma, 1985). The Harvard air pollution health study (Ferris *et al.*, 1979) has implemented a survey to investigate a relation between daily acidity and respiratory symptoms. Approximately 300 children in six U.S. cities will be followed for a year with self-administered calendars of respiratory symptoms. In

this paper, we propose a sensitive and inexpensive method to measure aerosol acidity using available equipment and relatively unskilled field technicians. We describe the development of an NH_3 diffusion denuder to protect the aerosol sample from neutralization during collection and a procedure for protecting the samples from NH_3 during shipping and analysis. Also, to increase the sensitivity of the analysis, this paper suggests extraction of the aerosol sample in a small solution volume, 3 ml, with the use of a microelectrode for pH determination. Finally, it presents and discusses results for strong acidity and sulfate concentrations, collected during a nine-month study in St Louis, Missouri and Kingston, Tennessee.

SAMPLING AND ANALYSIS

Sample collection

The Harvard impactor was used to collect aerosol particles with aerodynamic diameter below 2.5 μm (Turner *et al.*, 1985). The pump unit maintains the required flow of 4 ℓ min^{-1} within 5%, independent of outside temperature and filter loading, up to at least 152 cm of water pressure. The 7-day timer in the unit allows programmed start and end times for the 24-h sample collection period. Flow is measured prior to sample collection, but not at the end, because the required removal of the inlet tube would allow ambient NH_3 to neutralize the collected sample.

Samples are collected on 2-μm pore Teflon [PTFE] membrane filters, chosen for low blank acid and sulfate concentrations, bonded to 5.08 × 5.08 cm polyvinyl chloride square holders (Gelman Sciences Cat. No. SP2J03725). At the sampler entrance, air passes through a diffusion denuder coated with citric acid/glycerol, which removes ambient NH_3. The denuder is constructed using Al foil laminate honeycomb (foil thickness 0.051 mm; hexagonal cells 0.635 cm; length 5.08 cm; purchased from American Cyanamid), inside the cylindrical sampler inlet tube, i.d. 3.81 cm. Assuming that the honeycomb is the equivalent of 30 cylindrical tubes, we estimated the theoretical efficiency of NH_3 removal using the following formula (Gormley and Kennedy, 1949):

$$c/c_0 = [0.819][\exp(-14.6272\Delta)]$$

where $$\Delta = \pi DL/4F$$

and D = diffusion coefficient of ammonia in air = 0.236 cm^2 s^{-1}

L = length of tube = 5.08 cm

F = flow = 4/30 ℓ min^{-1} = 2.22 cm^3 s^{-1}.

The calculated value of c/c_0 is 0.0017, corresponding to an efficiency of 99.8% at 4 ℓ min^{-1}. The range of ambient NH_3 concentrations is usually 0.01–20 ppb (Lau and Charlson, 1977; Harward *et al.*, 1982). Assuming a value of 20 ppb NH_3, the amount that will penetrate the denuder is 0.04 ppb. This amount could neutralize 0.2 μg H_2SO_4 m^{-3}, an acceptably small loss. To retain more of the NH_3 trapping coating and thus achieve maximum capacity, the honeycomb surface is etched with ethanolic KOH. The denuder is coated using an ethanol solution containing 4% (w/v) citric acid monohydrate and 3% (w/v) glycerol. The capacity was measured by passing 4 ppm NH_3 in nitrogen through denuders at 4 ℓ min^{-1} until a breakthrough of NH_3 was detected, using a chemiluminescent NO_x monitor (ThermoElectron Corp. Model 14B/E) with an NH_3-to-NO converter. For a typical denuder, the breakthrough time was 40 min. Thus the capacity is equivalent to about 110 ppb NH_3 for 24 h, at 4 ℓ min^{-1}. Again, since daily mean ambient levels of NH_3 rarely exceed 20 ppb, the denuder has adequate capacity for our 24-h outdoor samples. Finally, chamber tests with cigarette smoke, which has a particle size distribution similar to ambient sulfate aerosol (Hinds, 1978), proved that no particles in the respirable size range are lost in the diffusion denuder.

Sample protection after collection

When the impactor is disconnected from the pumping unit at the sample collection site, caps are placed on both the inlet and outlet ports. After transport to the field laboratory, the sealed impactor is placed inside an ammonia-free glove box. The glove box has a citric acid-coated filter paper (Whatman No. 1) placed on the floor which removes NH_3 by diffusion. With the impactor inside the glove box, the filter holder is removed and placed inside a small polystyrene plastic box. To protect the sample from NH_3, two small squares (5.08 × 5.08 cm) of citric acid-coated cellulose filter paper are placed inside the small plastic box, separated from the sample filter by 1.6-mm-thick polyvinyl chloride plastic spacers, with one uncoated cellulose filter square below the coated squares. For shipment back to the central laboratory for analysis, the small plastic boxes are placed inside a polystyrene foam box, with additional pieces of citric acid-coated filter paper protecting the samples. At the central laboratory, the filters are kept inside the polystyrene foam shipping box until ready for pH analysis. At the time of preparation for extraction, the small polystyrene boxes are removed from the shipping box and placed inside an ammonia-free hood. Citric acid-coated glass wool removes ammonia and ambient particles from the supply air to the hood.

To test the protection methodology, sets of control filters were doped with the equivalent of 0.43 and 0.85 μg H_2SO_4 m^{-3}, for a 24-h, 4-ℓ min^{-1} sample. These values correspond to the two lowest concentration analytical standards. A total of 220 sets of controls were shipped to the field and back. The mean loss was only 0.06 ± 0.06 μg H_2SO_4 m^{-3} equivalent.

pH analysis

Inside the hood, the membrane is cut from its holder and placed inside a 4-ml polystyrene cup. Since the filter membrane material, PTFE Teflon, is hydro-

phobic, 0.100 ml of ethanol is used to wet the filter (Wolfson, 1980). Then 3 ml of the aqueous extraction solution, 10^{-4} N perchloric acid and 0.04 M KCl is added to the cup. In this pH range, aerosol weak acids and dissolved CO_2 have a negligible effect on the measured acidity. KCl is used to increase the ionic strength of the extract. The capped cups are sonicated for 15 min. The cup holder is rotated 90° each 5 min to achieve uniform sonication in a 0.95-ℓ ultrasonic bath. A small piece of polymethylmethacrylate plastic is placed in the bath to absorb excess energy. Two 1-ml aliquots of extract are transferred to 2-ml sample cups for pH analysis. The residual 1 ml is stored at 5°C for subsequent sulfate analysis. Using H_2SO_4, hydrogen ion standards are prepared in a range equivalent to 0–550 nmole $H^+ m^{-3}$, for 24 h at 4 ℓ min^{-1}. The standards are prepared by adding 0.100 ml of relatively concentrated solution of H_2SO_4 in ethanol to 3 ml of extraction solution. Blank solvent is prepared with the same ratio of pure ethanol to extraction solution. The pH determinations are made using an Orion Model 611 pH meter with a Fisher Scientific Model E-5M combination micro-electrode. The pH of standards and filter extracts is tested using one 2-ml cup containing 1 ml of solution to rinse the electrode and using a second 2-ml cup to determine pH. Two 2-ml cups of the blank solvent are measured between each test; the first is used for rinsing the electrode and the second is used as a control. For each standard and each filter extract, the apparent hydrogen ion concentration, $[H^+]$, is calculated as follows:

$$[H^+] = 10^{-pH} - 10^{-pHb}$$

where pH and pHb are, respectively, the pH of the test solution and the blank solvent.

The apparent concentrations differ slightly from true concentrations because of ionic strength effects due to the 0.04 M KCl, and also possibly due to the approximately 3% ethanol. Apparent concentrations were regressed on actual standard concentrations and the resulting slope is used to determine actual H_2SO_4 equivalent concentrations for the ambient air filter extracts. To test for matrix effects of the filter material, a comparison was made with standards prepared by doping filters with H_2SO_4, and extracting them using the same method as with filters containing ambient air samples. The strong acid concentrations determined for the doped filter standards were about 3% lower than those for routine standards. Since routine standards are prepared without filters, a correction is made for this difference when calculating the concentrations for filter extracts. Final sample concentrations are determined based on actual flow and sample times. The estimated minimum detectable concentration is 2 nmole H_2SO_4 m^{-3} (0.2 μg sulfuric acid m^{-3}) for 24-h samples at 4 ℓ min^{-1}. Sulfate is measured using the methylthymol blue method on the Technicon AutoAnalyzer II (McSwain and Watrous, 1974).

To validate our extraction procedure, we regressed sulfate concentrations obtained from the above technique on elemental sulfur concentrations determined by X-ray fluorescence (Dzubay and Stevens, 1975). The estimated slope is 2.9 ± 0.2, $n = 25$. This result is in good agreement with the mass ratio of sulfate to elemental sulfur, 3.0. The intercept is -866 ± 489 ng m^{-3} and the correlation coefficient, r^2, is 0.87.

Description of the sampling sites

St Louis, Missouri is one of the six cities involved in our prospective epidemiological study of air pollution and respiratory health (Ferris *et al.*, 1979). The operation of the Regional Air Pollution Study (RAPS) site 111 in the southeast section of the city was taken over by our study in 1978. While the immediate area is residential and light commercial, railroad tracks border the site and there are several industrial facilities including a coke plant, sludge incinerator and secondary metal processing plants within 6.4 km. A bottle crushing/recycling operation is located roughly 0.4 km N of the sampling site.

Kingston, Tennessee is also one of the six cities participating in our epidemiological study. This town is located in the Tennessee Valley, about 60 km SW of Knoxville. The major source is a nearby 1500-MW coal-fired electric generating plant, operated by the Tennessee Valley Authority (TVA). All emissions are discharged through two 300-m stacks. Also, in the immediate vicinity are a steam plant and a cement facility.

RESULTS

Figures 1(c) and 2(c) illustrate the variation in daily sulfate concentrations, during the period of December 1985 to August 1986, in St Louis, Missouri, and Kingston, Tennessee, respectively. Both sites show higher concentrations of sulfates during the summer. However, several sulfate events were observed in both the winter and spring season. Higher sulfate concentrations in the summer have been observed consistently in urban, industrial and rural areas because of the higher oxidation rates of SO_2 to SO_4^{2-} (Altshuller, 1984). In addition, the longer lifetime of sulfates in the atmosphere during dry periods can result in higher sulfate concentration levels (Rhode and Grandell, 1981). Figure 3 compares the sulfate concentration distributions in St Louis and Kingston. These results reveal that the nine-month average concentration is slightly higher in Kingston, 73.6 nmole m^{-3}, compared to that in St Louis, 61.6 nmole m^{-3}.

Figures 1(b) and 2(b) illustrate the variation in daily hydrogen ion concentration, in nmole m^{-3}, in St Louis and Kingston, respectively. In St Louis, hydrogen ion concentrations are very low during the winter and spring, and relatively higher in the summer. In Kingston, although there is a similar seasonal pattern to that in St Louis, concentrations are considerably higher during the entire period. The distribution of

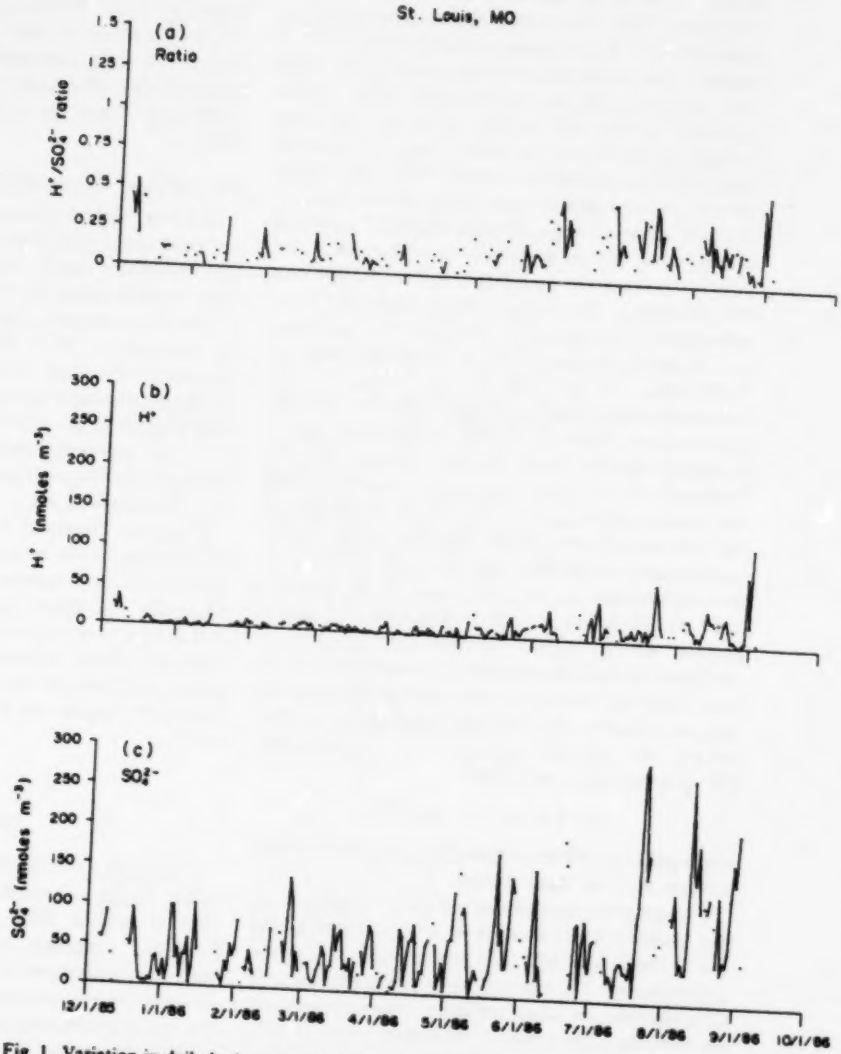

Fig. 1. Variation in daily hydrogen and sulfate ion concentrations and their ratio in St Louis, Missouri. (a) Ratio. (b) Hydrogen ion concentration. (c) Sulfate ion concentration.

hydrogen ion concentrations at these sites is shown in Fig. 3. The mean hydrogen ion concentrations in Kingston and St Louis are 36.1 and 10.3 nmole m^{-3}, respectively.

Figures 1(a) and 2(a) show the variation in the daily molar ratios of H^+/SO_4^{2-} in St Louis and Kingston, respectively. Molar ratios equal to 0.0, 0.5, 1.0 and 2.0 correspond to compositions of ammonium sulfate, $[NH_4]_2SO_4$, letovicite, $[NH_4]_3H[SO_4]_2$, ammonium bisulfate, NH_4HSO_4 and H_2SO_4, respectively. These results indicate that in St Louis sulfates are mostly in the composition range of ammonium sulfate to letovicite. The nine-month average molar ratio of H^+/SO_4^{2-} is equal to 0.18. In Kingston, sulfate composition is usually in the range between ammonium sulfate and ammonium bisulfate. The nine-month average molar ratio of H^+/SO_4^{2-}, 0.45, is higher than that found in St Louis.

CONCLUSIONS

This paper presents an improved method for measuring aerosol strong acidity. Samples are adequately protected from neutralization by ambient NH_3 during collection, shipping and analysis. Use of a small volume of extraction solution, 3 ml, and a pH micro-electrode allow for a maximum sensitivity. The estimated detection limit for a 4-ℓ min^{-1}, 24-h sample is 0.2 μg H_2SO_4 m^{-3} equivalent. Due to its sensitivity and relatively low cost, the method described in this paper could be very useful in conducting acid aerosol studies.

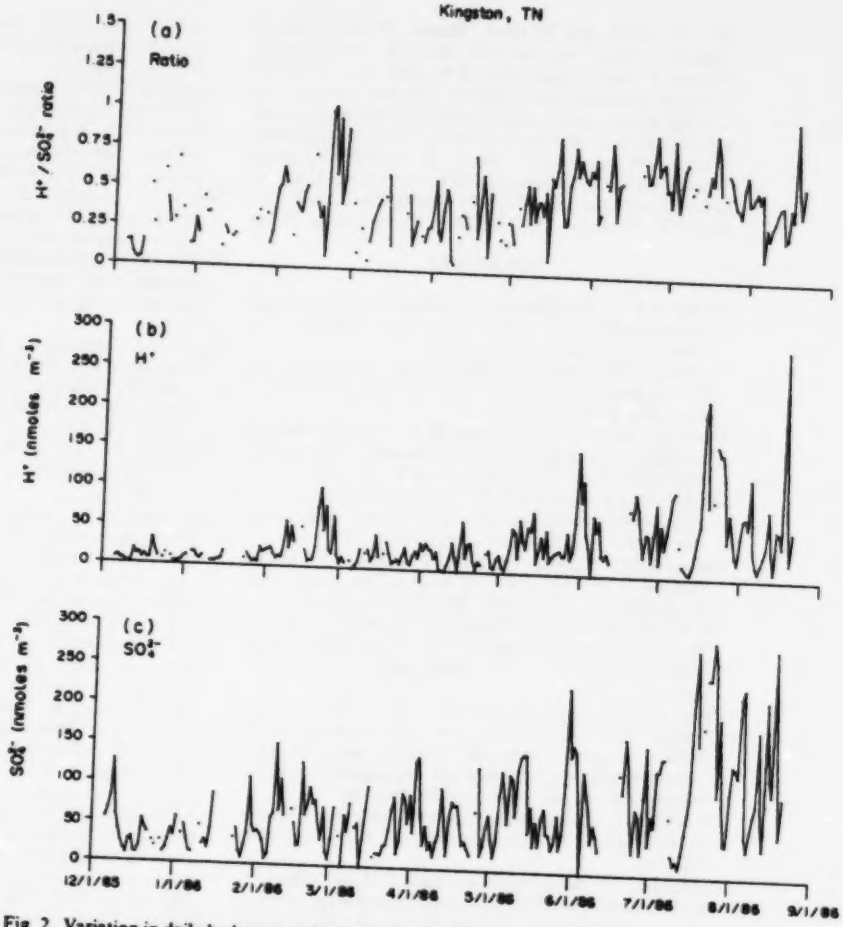

Fig. 2. Variation in daily hydrogen and sulfate ion concentrations and their ratio in Kingston, Tennessee. (a) Ratio. (b) Hydrogen ion concentration. (c) Sulfate ion concentration.

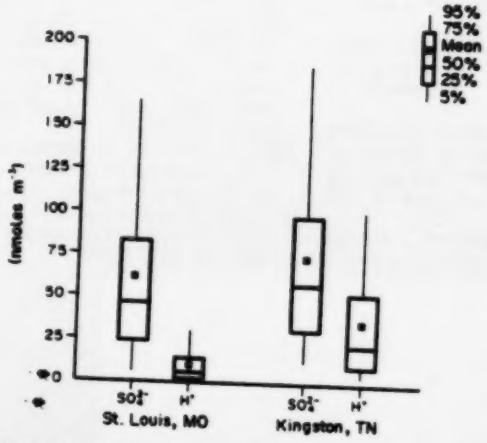

Fig. 3. Distribution of sulfate and hydrogen ion concentrations in St Louis, Missouri and Kingston, Tennessee.

The results from the nine-month study in St Louis and Kingston show regional and seasonal variations in aerosol strong acid concentrations. Aerosols were more acidic in the summer. Although the two cities had similar sulfate mean concentrations, the acidity for Kingston was much higher. This may be explained by the fact that St Louis is more urban. Ammonium nitrate, which is an important component of ambient fine aerosol in urban areas, could displace hydrogen ion from the collected acidic sulfate particles. To compensate for this artifact, we are currently developing a sampling method which will allow determination of the amount of displaced strong acidity.

These corrections, along with ambient ammonia concentration measurements, will finally make possible a thorough understanding of sources and atmospheric processes affecting aerosol acidity.

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